

**US-PAT-NO:**

6383386

**DOCUMENT-  
IDENTIFIER:**

US 6383386 B1

**TITLE:**

Hydrophobic permeable composite, method for producing said  
composite and use of the same

**DATE-ISSUED:**

May 7, 2002

**INVENTOR-INFORMATION:**

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**APPL-NO:** 09/463413

**DATE FILED:** March 10, 2000

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DE	198 24 666	June 3, 1998

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CIPS	<u>B01 D 46/48</u> 20060101
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CIPS	<u>B01 J 35/00</u> 20060101
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CIPS	<u>B01 D 46/24</u> 20060101
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**US-CL-ISSUED:** 210/500.25 , 210/500.26 , 210/490 , 210/500.27 , 55/523 , 55/524 , 264/42 , 264/45.5

**US-CL-CURRENT:** 210/500.25 , 210/490 , 210/500.26 , 210/500.27 , 264/42 , 264/45.5 , 55/523 , 55/524

**FIELD-OF-CLASSIFICATION-SEARCH:** 210/500.25; 210/500.26 ; 210/490 ; 210/500.27 ; 210/500.36 ; 210/500.41 ; 210/500.2 ; 55/523 ; 55/524 ; 264/42 ; 264/45.5

**\*\*See application file for complete search history\*\***

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## U.S. PATENT DOCUMENTS

### PAT-NO ISSUE-DATE PATENTEE-NAME US-CL

<u>4321141</u>	March 1982	Messing	N/A	N/A N/A
<u>4609468</u>	September 1986	Gramm	N/A	N/A N/A
<u>4981590</u>	January 1991	Van T'Veen et al.	N/A	N/A N/A
<u>5059366</u>	October 1991	Galaj	N/A	N/A N/A
<u>5124289</u>	June 1992	Martin et al.	N/A	N/A N/A
<u>5266207</u>	November 1993	Bayce et al.	N/A	N/A N/A
<u>5342521</u>	August 1994	Bardot et al.	N/A	N/A N/A
<u>5376442</u>	December 1994	Davidson et al.	N/A	N/A N/A
<u>5885657</u>	March 1999	Penth	N/A	N/A N/A

## FOREIGN PATENT DOCUMENTS

### FOREIGN-PAT-NO PUBN-DATE COUNTRY US-CL

2014868	September 1979	GB
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**ART-UNIT:** 1723

**PRIMARY-EXAMINER:** Fortuna; Ana

**ATTY-AGENT-FIRM:** Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

## ABSTRACT:

The invention relates to a hydrophobic permeable composite, to a method for producing a hydrophobic permeable composite and to the use of said composite in various processes. Hydrophobic, permeable materials have been known for some time. Plastic materials especially, for example Gore-Tex.RTM., but also materials consisting of other organic polymers are used whenever a material is required to be gas- and steam-permeable but not liquid-permeable. These materials have the disadvantage that they can only be used within a certain temperature range. The inventive composite is characterised by a higher temperature resistance since it consists mainly of inorganic materials. It is also relatively easy to produce since it can be obtained using the sol-gel technique. The inventive composite can be used as a membrane in the oxidation of aromatics, for example in the direct oxidation of benzene to phenol.

35 Claims, 1 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 1

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**Brief Summary Text - BSTX (15):**

Preferably the interior and exterior or the interior and the exterior surfaces of the composite material according to the invention are coated with hydrophobic layers. These layers can contain at least alkyl, fluoroalkyl and/or aryl groups. The interior and/or exterior surfaces of the composite material can also be coated, however, with wax and/or polymer layers. The polymer layers can contain hydrophobic materials chosen from polyethylene, polyvinyl chloride, polystyrene, polytetrafluoroethylene, polyvinylidene fluoride, polyvinylidene chloride, polyisoprene, polybutadiene, heat-treated **polyimide**, heat-treated polyether imide, polysulfone, polyether sulfone, polyacrylate, polyimidazole or a mixture of these polymers. Preferably the hydrophobic material present in the hydrophobic layers has a melting and/or softening point below 500.degree. C.

**Brief Summary Text - BSTX (21):**

The composite material according to the invention is preferably provided with at least one support which contains at least aluminum, **silicon**, cobalt, manganese, zinc, vanadium, molybdenum, indium, lead, bismuth, silver, gold, nickel, copper, iron, titanium, platinum, stainless steel, steel, brass, an alloy of these materials or a material coated with Au, Ag, Pb, Ti, Ni, Cr, Pt, Pd, Rh, Ru and/or Ti.

**Brief Summary Text - BSTX (36):**

The sols are obtained by hydrolyzing at least one compound, preferably at least one metal compound, at least one semi-metal compound or at least one mixed-metal compound with at least one liquid, one solid or one gas, in which process it can be advantageous if water, alcohol or an acid, for example, is used as the liquid, ice as the solid or steam as the gas, or if at least one combination of these liquids, solids or gases is used. It can also be advantageous to add the compound to be hydrolyzed to alcohol or an acid or a combination of these liquids before hydrolysis. As the compound to be hydrolyzed there is preferably hydrolyzed at least one metal nitrate, one metal chloride, one metal carbonate, one metal alcoholate compound or at least one semi-metal alcoholate compound, especially preferably at least one metal alcoholate compound, one metal nitrate, one metal chloride, one metal carbonate or at least one semi-metal alcoholate compound chosen from the compounds of the elements Ti, Zr, Al, Si, Sn, Ce

and Y or of the lanthanoids and actinoids, such as titanium alcoholates, for example titanium isopropylate, **silicon** alcoholates, zirconium alcoholates, or a metal nitrate, such as zirconium nitrate.

#### **Brief Summary Text - BSTX (46):**

In a special embodiment of the process according to the invention, the permeable composite material which exhibits hydrophobic properties can be made by using, in the process for making a permeable composite material described hereinabove and in PCT/EP98/05939 a sol and/or a suspension to which finely divided waxes and/or polymers are added. During solidification of the sol or of the suspension, the waxes and/or polymers are melted at temperatures below 500.degree. C. and surround the particles as a thin film, so that the entire interior and exterior surface of the composite material is covered by a thin wax and/or polymer layer. For this purpose there can be used almost all known polymers or waxes which melt and/or can flow below 500.degree. C., such as polyethylene, polypropylene, polyvinyl chloride, polystyrene, polytetrafluoroethylene, polyvinylidene fluoride, polyvinylidene chloride, polyisoprene, polybutadiene, **polyimide**, polyether imide, polysulfone, polyether sulfone, polyacrylate, polymethacrylate, polyimidazole or a mixture of these polymers. The waxes and/or polymers do not have to exist as hydrophobic materials, but it is completely adequate when they acquire the hydrophobic properties during the heating phase at a temperature of up to 500.degree. C. by a chemical and/or physical modification of their structure.

#### **Detailed Description Text - DETX (32):**

80 g of titanium tetraisopropylate was hydrolyzed with 20 g of water, and the resulting precipitate was peptized with 120 g of nitric acid (25%). This solution was stirred until it became clear and, after addition of 40 g of titanium **dioxide** from Degussa (P25) and 5 g of polytetrafluoroethylene powder, stirring was continued until disintegration of the agglomerates. This suspension was then applied on a porous support corresponding to Example 1.1 and solidified at 500.degree. C. within the shortest possible time.

#### **Detailed Description Text - DETX (41):**

80 g of titanium tetraisopropylate was hydrolyzed with 20 g of water, and the resulting precipitate was peptized with 120 g of nitric acid (25%). This solution was stirred until it became clear and, after addition of 40 g of titanium **dioxide** from Degussa (P25) and 15 g of **polyimide** powder, stirring was continued until disintegration of the agglomerates. This suspension was then applied on a porous support corresponding to Example 1.1 and solidified at 500.degree. C. within the shortest possible time. In this case good hydrophobing is achieved only after complete transformation (carbonization and imidization) of the **polyimide**.

## Detailed Description Paragraph Table - DETL (1):

Example Hydrophobing component Contact angle [.degree.] 1.1 -- 0 1.2.a. Dynasilan F 8261 145 1.2.b Methyltriethoxysilane 136 1.3.a.1 Dynasilan F 8261 139 1.3.a.2 Methyltriethoxysilane 134 1.3.a.3 i-Butyltriethoxysilane 110 1.3.b.1 Dynasilan F 8261 141 1.3.b.2 Methyltriethoxysilane 134 1.3.b.3 i-Butyltriethoxysilane 109 1.4.a.1 Polytetrafluoroethylene 148 1.4.a.2 Polyethylene 132 1.4.a.3 Polypropylene 136 1.4.b **Polyimide** 108

## Claims Text - CLTX (7):

6. The composite material according to claim 2, wherein the hydrophobic layers contain at least one hydrophobic material selected from the group consisting of polyethylene, polypropylene, polyvinyl chloride, polystyrene, polytetrafluoroethylene, polyvinylidene fluoride, polyvinylidene chloride, polyisoprene, polybutadiene, heat-treated **polyimide**, heat-treated polyether imide, polysulfone, polyether sulfone, polyacrylate, polymethacrylate, polyimidazole and a mixture of these polymers.

## Claims Text - CLTX (24):

23. A process according to claim 11, wherein the hydrophobic material is, selected from polyethylene, polypropylene, polyvinyl chloride, polystyrene, polytetrafluoroethylene, polyvinylidene fluoride, polyvinylidene chloride, polyisoprene, polybutadiene, **polyimide**, polyether imide, polysulfone, polyether sulfone, polyacrylate, polymethacrylate, polyimidazole or a mixture of these polymers.

## Current US Cross Reference Classification - CCXR (1):

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Chng; Mei Lin	Singapore	N/A	N/A	SG
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**TYPE**

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528/480, 210/500.39 , 525/436 , 528/353 ,  
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**FIELD-OF-CLASSIFICATION-  
SEARCH:**

528/353; 528/480 ; 95/43 ; 96/14 ; 525/436 ;  
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**\*\*See application file for complete search history\*\***

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**U.S. PATENT DOCUMENTS**

**PAT-NO ISSUE-DATE PATENTEE-NAME US-CL**

<u>4717393</u>	January 1988	Hayes	55/16
<u>4981497</u>	January 1991	Hayes	55/16
<u>6639042</u>	October 2003	Baek et al.	528/170

**FOREIGN PATENT DOCUMENTS**

**FOREIGN-PAT-NO PUBN-DATE COUNTRY US-CL**

WO 99/40996	August 1999	WO	N/A
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M. Al-Masri, H. R. Kricheldorf, D. Fritsch, New **polyimides** for gas separation, 1. **polyimides** derived from substituted terphenylenes and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, Macromolecules, 32 (1999) 7853. cited by other

W. J. Koros, R. Mahajan, Pushing the limits on possibilities for large scale gas separation: which strategies?, J. Membr. Sci. 175 (2000) 181. cited by other

A. Bos, I. G. M. Punt, M. Wessling, H. Strathmann, Suppression of CO<sub>2</sub>-plasticization by semi-interpenetrating polymer network formation, J. Polym. Sci., Part B: Polym. Phys. 36 (1998) 1547. cited by other

**ART-UNIT:** 1711

**PRIMARY-EXAMINER:** Boykin; Terressa

**ATTY-AGENT-FIRM:** Klarquist Sparkman, LLP.

#### **ABSTRACT:**

The present invention deals with a process for treating a **polyimide** comprising exposing said **polyimide** to a compound selected from the group consisting of dendrimers, hyperbranched polymers and mixtures thereof. The **polyimide** may be in the form of a membrane and the membrane, after treatment according to the process of the invention, may be suitable for use in a membrane-based separation technique, for example gas separation, filtration, microfiltration, ultrafiltration, reverse osmosis or pervaporation. The membrane may for example be suitable for separation of gas and hydrocarbon mixtures including mixtures of H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CO<sub>2</sub>, He/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and C<sub>2</sub> C<sub>4</sub> hydrocarbon mixtures.

14 Claims, 5 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 4

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**Abstract Text - ABTX (1):**

The present invention deals with a process for treating a polyimide comprising exposing said polyimide to a compound selected from the group consisting of dendrimers, hyperbranched polymers and mixtures thereof. The polyimide may be in the form of a membrane and the membrane, after treatment according to the process of the invention, may be suitable for use in a membrane-based separation technique, for example gas separation, filtration, microfiltration, ultrafiltration, reverse osmosis or pervaporation. The membrane may for example be suitable for separation of gas and hydrocarbon mixtures including mixtures of H.sub.2/N.sub.2, H.sub.2/CO.sub.2, He/N.sub.2, CO.sub.2/CH.sub.4, and C2 C4 hydrocarbon mixtures.

**TITLE - TI (1):**

Polyimide membranes

**Brief Summary Text - BSTX (2):**

The present invention relates to a process for treating polyimides, and to membranes comprising polyimides treated by said process. It further relates to a method for separation of gases using said membranes.

**Brief Summary Text - BSTX (4):**

Polymeric membrane materials for gas separation should not only have good gas separation properties, for example high gas permeability and permselectivity, but should also maintain their intrinsic gas separation properties in complex and harsh environments. Polyimides are attractive membrane materials for gas separation because of their good gas separation and physical properties. Many attempts have been made to modify the chemical structure of polyimides with the aim of obtaining both highly permeable and permselective membrane materials. However most of the polyimides produced either have relative low selectivity or suffer severe ageing and performance decay due to densification and/or plasticization. In order to overcome these problems, cross-linking modifications have been carried out.

#### **Brief Summary Text - BSTX (5):**

Results suggest that cross-linking provides membranes with anti-plasticization properties and good chemical resistance. In addition, the gas permeability/permeability relationships of some cross-linked polyimides were higher than the normal trade-off line.

#### **Brief Summary Text - BSTX (6):**

Cross-linking of polyimides can be effected by several methods. For example, one method uses UV light induced photochemical cross-linking reactions in benzophenone-containing polyimides, however the difficulty of implementing the method uniformly on hollow fibre membranes limits its application. Another method uses the formation of semi-interpenetrating networks using polymeric blends, and subsequent thermal treatment at elevated temperatures. This method has the potential to yield materials with better anti-plasticization characteristics, however heat treatment is time consuming and is not a preferred process economically. Copolyimides containing strong polar carboxylic acid groups may exhibit reduced plasticization due to hydrogen bonding between the carboxylic acid groups. However, cross-linking reactions between ethylene glycol and carboxylic acid groups in diaminobenzoic acid (DABA) based polyimides commonly occur at around 150.degree. C. A disadvantage of heat treatment at elevated temperatures is the deterioration of the subtle structures of asymmetric membranes and impairment of their gas permeation properties.

#### **Brief Summary Text - BSTX (8):**

To date, the only simple, practical chemical cross-linking method to modify 6FDA-polyimide asymmetric hollow fibers has been performed by Liu, Wang and Chung (Y.

#### **Brief Summary Text - BSTX (9):**

Liu, R. Wang, T. S. Chung, "Chemical cross-linking modification of polyimide membranes for gas separation", J. Membr. Sci., 189 (2001) 231). Their process involves immersing fibers into a p-xylenediamine or m-xylenediamine/methanol solution for a short period of time at ambient temperature.

#### **Brief Summary Text - BSTX (13):**

In a first aspect of the invention there is provided a process for treating a polyimide comprising exposing said polyimide to a compound selected from the group consisting of dendrimers, hyperbranched polymers and mixtures thereof.

#### **Brief Summary Text - BSTX (14):**

The **polyimide** may be in the form of a membrane. The compound may comprise a plurality of amine groups, and at least two amine groups per molecule of said compound may be primary amine groups. The compound may crosslink the membrane. The dendrimer may be a polypropyleneimine dendrimer, and may be of generation up to 4. The **polyimide** may be an aromatic **polyimide**. The process may comprise dissolving the compound in a first solvent, and the concentration of the compound in the first solvent may be between about 1 wt % and about 30 wt %. The process may be conducted at a temperature below about 100.degree. C. Following exposure of the membrane to the compound, the membrane may be washed with a second solvent and may then be dried.

#### **Brief Summary Text - BSTX (15):**

There is also provided a **polyimide** when obtained by the process of the first aspect, and there is also provided a membrane comprising said **polyimide**.

#### **Description Paragraph - DETX (2):**

FIG. 1 shows a FTIR-ATR spectra of a 6FDA-Durene **polyimide** membrane film before and after cross-linking with a DAB dendrimer;

#### **Description Paragraph - DETX (3):**

FIG. 2 shows a graph of gel content (%) vs. cross-linking time (min) of cross-linked 6FDA-Durene **polyimide** membrane films resulting from different generations of DAB dendrimers;

#### **Description Paragraph - DETX (5):**

FIG. 4(a) shows a graph of H.sub.2/N.sub.2 selectivity vs. H.sub.2 permeability for G1 cross-linked 6FDA-Durene **polyimide** membrane film; and

#### **Description Paragraph - DETX (6):**

FIG. 4(b) shows a graph of H.sub.2/N.sub.2 selectivity vs. H.sub.2 permeability for G2 and G3 cross-linked 6FDA-Durene **polyimide** membrane films.

#### **Description Paragraph - DETX (8):**

The present invention relates to treatment of **polyimides** in order to confer improved chemical resistance, anti-plasticization characteristics and permselectivity relative to uncross-linked **polyimides**, by using suitable dendrimers (which may consist of multifunctional amines) as cross-linking reagents.

#### **Description Paragraph - DETX (9):**

There is described herein a process for treating a **polyimide** membrane comprising exposing the membrane to a compound selected from the group consisting of dendrimers, hyperbranched polymers and mixtures thereof, wherein the compound comprises a plurality of amine groups, said compound being dissolved in a solvent under conditions whereby said compound crosslinks said membrane.

#### **Description Paragraph - DETX (10):**

The **polyimides** of the invention are commonly in the form of membranes. The membranes may be gas separation membranes, microporous membranes, ultrafiltration membranes, reverse osmosis membranes or some other type of membrane, and they may be suitable for use in a membrane-based separation technique, for example gas separation, filtration, microfiltration, ultrafiltration, reverse osmosis or pervaporation. They may for example be suitable for separation of gas and hydrocarbon mixtures including mixtures of H.sub.2/N.sub.2, H.sub.2/CO.sub.2, He/N.sub.2, CO.sub.2/CH.sub.4, and C2-C4 hydrocarbon mixtures. The membranes may be in the form of dense films, asymmetric hollow fibres, dual layer hollow fibres, composite membranes of **polyimides** or other suitable form.

#### **Description Paragraph - DETX (11):**

The **polyimide** may be an aromatic **polyimide** or a partially aromatic **polyimide** or a nonaromatic **polyimide**. In particular, an aromatic **polyimide** suitable for use in the present invention may comprise the following structural unit:

#### **Description Paragraph - DETX (15):**

##STR00004## wherein Z has the same meaning as defined above, and X, X.sub.1, X.sub.2 and X.sub.3 are independently selected from the group consisting of hydrogen, allyl groups with 1 to 5 carbon atoms, alkoxy groups with 1 to 5 carbon atoms, phenyl groups, substituted phenyl groups, phenoxy groups and substituted phenoxy groups; and n is a number sufficient that said aromatic **polyimide** has an inherent viscosity of at least 0.3 dl/g when measured at 25.degree. C. using a 0.5% by weight solution in N-methylpyrrolidinone. The aromatic **polyimide** may be selected from the group consisting of: 1) **polyimides** comprising groups derived from benzophenone tetracarboxylic anhydride dianhydride (BTDA), methylene diisocyanate (MDI) and toluene diisocyanate (MDI), (available commercially as **polyimide** P84 from Lenzing) and 2) **polyimides** of structure:

#### **Description Paragraph - DETX (17):**

The compounds of the present invention, used in treating a **polyimide**, are selected from the group consisting of dendrimers, hyperbranched polymers and mixtures thereof,

and may comprise a plurality of amine groups. At least two amine groups per molecule of said compound may be primary amine groups. The dendrimer may be a polypropyleneimine dendrimer, and may be of generation up to 4, and may be generation 1, 2, 3 or 4, or may be generation greater than 4. These dendrimers have a high density of primary amino groups suitable for crosslinking a polyimide according to the process of the invention.

#### **Description Paragraph - DETX (20):**

The process for treating a polyimide according to the present invention comprises exposing the polyimide to a compound which is a dendrimer, a hyperbranched polymer or a mixture thereof, and may comprise dissolving the compound in a first solvent before is said exposing. The first solvent may be an alcohol, for example methanol, ethanol, propanol, isopropanol, n-butanol, isobutanol or some other convenient alcohol. Other solvents that may be used include for example ketones such as acetone or methylethylketone, ethers such as diethyl ether, esters such as ethyl acetate or other solvents known to those skilled in the art. The concentration of the compound in the first solvent may be between about 1 wt % and about 50 wt %, or between about 2 and 40 wt % or between about 3 and 30 wt % or between about 4 and 20 wt % or between about 5 and 10%, or may be about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45 or 50 wt %. The process may be conducted at about ambient temperature or at a temperature below about 100.degree. C., or below about 80.degree. C., or below about 60.degree. C. or below about 40.degree. C., or between about 0 and 100.degree. C. or between about 10 and 80.degree. C. or between about 20 and 60.degree. C. or between about 30 and 50.degree. C., and may be conducted at about 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 or 100.degree. C. The step of exposing may comprise immersing the polyimide in the compound or in a solution of the compound, or it may comprise passing the compound or a solution of the compound over the polyimide, or it may comprise spraying the polyimide with the compound or a solution of the compound, or it may comprise exposing the polyimide to the vapour of the compound, or it may comprise some other convenient method. The time of the exposure may be between about 1 second and 300 minutes, or between about 2 seconds and 270 minutes or between about 5 seconds and 240 minutes or between about 10 seconds and 210 minutes or between about 15 seconds and 180 minutes or between about 30 seconds and 150 minutes or between about 1 and 120 minutes or between about 2 and 100 minutes, or between about 5 and 80 minutes or between about 10 and 70 minutes or between about 15 and 60 minutes or between about 20 and 55 minutes or between about 25 and 50 minutes or between about 30 and 45 minutes, and may be about 1, 2, 5, 10, 15, 30 or 45 seconds, or about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, 80, 90, 100, 120, 140, 160, 180, 200, 250 or 300 minutes, or it may be greater than 300 minutes. Following exposure of the membrane to the compound for an appropriate time, the membrane may be washed with a second solvent and may then be dried. Commonly the second solvent is an

alcohol, and may be the same as the first solvent, or it may be a different solvent. Commonly the second solvent will be methanol, ethanol, propanol, isopropanol, n-butanol or isobutanol however other alcohols may be used. Other solvents that may be used include for example ketones such as acetone or methylethylketone, ethers such as diethyl ether, esters such as ethyl acetate or other solvents known to those skilled in the art. Drying may conveniently be conducted in air, and may be at ambient temperature or may be at a temperature below about 100.degree. C., or below about 80.degree. C., or below about 60.degree. C. or below about 40.degree. C., or between about 0 and 100.degree. C. or between about 10 and 80.degree. C. or between about 20 and 60.degree. C. or between about 30 and 50.degree. C., and maybe conducted at about 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 or 100.degree. C. Drying may be conducted by keeping the polyimide at ambient pressure or by applying a vacuum, or it may comprise passing a stream of gas past, through or over the polyimide. The time required for drying the membrane will depend on the conditions used for drying and on the nature of the solvents used in the process of treating the polyimide. Commonly the time required for drying will be between about 30 minutes and 48 hours, or between about 1 and 40 hours, or between about 2 and 32 hours or between about 3 and 24 hours or between about 4 and 20 hours or between about 5 and 16 hours or between about 6 and 12 hours, and may be about 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 12, 16, 20, 24, 30, 36, 42 or 48 hours.

#### **Description Paragraph - DETX (23):**

A preferred process for treating a polyimide membrane according to the present invention comprises exposing the polyimide membrane to a polypropyleneimine dendrimer of generation between 1 and 3. The treatment process comprises dissolving the dendrimer in an alcohol, for example methanol, at a concentration of between about 5 wt % and about 30 wt %, and immersing the polyimide membrane in the a solution, which is kept at a temperature of between about 20 and 60.degree. C. The membrane is kept in the solution for between about 1 second and 60 minutes. The membrane is then washed with an alcoholic solvent and dried. Drying may conveniently be conducted in air for up to about 1 day, and is commonly conducted at ambient temperature, or at elevated temperatures for a few seconds to minutes.

#### **Description Paragraph - DETX (24):**

The membrane may then be mounted into a gas separation module. The conformation of the module will depend on the conformation of the treated polyimide membrane. For example, if the membrane is a flat sheet, the module may have a spiral wound configuration.

#### **Description Paragraph - DETX (27):**



The **polyimide** material and the dense film preparation employed in the examples are illustrated as follows.

#### **Description Paragraph - DETX (29):**

The chemical structure of 6FDA-Durene **polyimide** is shown above. It was synthesized by the method of J. H. Fang, H. Kita and K. Okamoto ("Hyperbranched **polyimides** for gas separation applications. 1. Synthesis and characterization", *Macromolecules*, 33 (2000) 4693). A 2% (w/w) polymer solution was prepared by dissolving the **polyimide** in dichloromethane. The polymer solution was then filtered through a Watman's filter (1  $\mu$ m) and cast onto a **silicon** wafer at ambient temperature. After slow solvent evaporation, the film was dried in a vacuum oven at 250.degree. C. for 48 h to remove the residual solvent.

#### **Description Paragraph - DETX (34):**

FTIR-ATR measurements were performed using a Perkin Elmer FT-IR Spectrometer Spectrum 2000 to estimate the extent of reaction between DAB dendrimers and **polyimide**. FIG. 1 presents the FTIR-ATR spectra before and after cross. **polyimide**. The following Figure presents the FTIR-ATR spectra before and after cross-linking with a DAB dendrimer. The original 6FDA-durene is characterized by bands at around 1782.5 cm.sup.-1 (attributed to C.dbd.O asymmetric stretch of imide groups), 1714.5 cm.sup.-1 (attributed to C.dbd.O symmetric stretch of imide groups), and 1350.9 cm.sup.-1 (attributed to C--N stretch of imide groups). After cross-linking, the C.dbd.O stretch band at around 1646.6 cm.sup.-1 of amide groups and the C--N stretching of the C--N--H group at around 1520.8 cm.sup.-1 were present. The intensities of characteristic imide peaks (at 1782.5 cm.sup.-1 and 1714.5 cm.sup.-1) decreased, and the intensities of characteristic amide peak (at 1646.6 cm.sup.-1) increased with the treatment time. This suggests that the degree of cross-linking increased with treatment time. The FTIR-ATR spectra of G2 and G3 dendrimers cross-linked films show similar trends.

#### **Description Paragraph - DETX (35):**

The gel contents of cross-linked **polyimide** membranes were measured by extracting the films in dichloromethane for 24 hrs. The insoluble fractions were vacuum dried at 120.degree. C. for about 1 day. The weights of **polyimide** films before and after extraction were measured and the gel content was calculated by:

#### **Description Paragraph - DETX (39):**

The pure gas permeabilities were determined by a constant volume and variable pressure is method. Detailed experimental design and procedures have been reported by A. Bos, I. G. M. Punt, M. Wessling and H. Strathmann ("Plasticization-resistant glassy

polyimide membranes for CO/CH separations", Separation and Purif. Tech 14 (1998) 27). The permeabilities were obtained in the order He, H.sub.2, O.sub.2, N.sub.2, CH.sub.4 and CO.sub.2 at 35.degree. C. The upstream pressure was 3.5 atm for He and H.sub.2 and 10 atm for the other gases.

#### **Description Paragraph - DETX (47):**

One of the novel aspects of this invention is the ability to achieve superior gas transport properties compared to other polymers. The gas transport properties of G1, G2 and G3 treated polyimide samples are compared with the upper bound materials (data from L. M. Robeson, "Correlation of separation factor versus permeability for polymeric membranes", J. Membr. Sci., 62(1991) 165). FIGS. 4(a) and (b) demonstrate that all treated 6FDA-durene samples showed excellent gas transport properties, which are above or near to the "upper bound materials". With an increase in cross-linking time, the gas transport properties are further improved and located well above the permselectivity-permeability trade-off line. This suggests that the proposed cross-linking method has great potential to improve polyimide materials for gas separation.

#### **Claims Text - CLTX (1):**

1. A process for treating a membrane of the type used in gas separation or pervaporation, the membrane comprising polyimide, the process comprising the steps of: (a) directly exposing said polyimide to a dendrimer in a solvent, and (b) maintaining said solvent containing said exposed polyimide and said dendrimer at a temperature of less than 100.degree. C. and for a time to allow the compound to crosslink the polyimide.

#### **Claims Text - CLTX (6):**

6. The process of claim 1 wherein the polyimide is an aromatic polyimide.

#### **Claims Text - CLTX (7):**

7. The process of claim 1 wherein the polyimide comprises the following structural unit: ##STR00009## wherein Ar.sub.1 is a tetravalent organic group selected from the group consisting of: ##STR00010## wherein Z is selected from the group consisting of: ##STR00011## Ar.sub.2 is an aromatic group selected from the group consisting of: ##STR00012## wherein Z has the same meaning as defined above, and X, X.sub.1, X.sub.2 and X.sub.3 are independently selected from the group consisting of hydrogen, alkyl groups with 1 to 5 carbon atoms, alkoxy groups with 1 to 5 carbon atoms, phenyl groups, substituted phenyl groups, phenoxy groups and substituted phenoxy groups; and n is a number sufficient that the polyimide has an inherent viscosity of at least 0.3 dl/g when measured at 25.degree. C. using a 0.5% by weight solution in N-methylpyrrolidinone.

### Claims Text - CLTX (8):

8. The process of claim 1 wherein the polyimide is selected from the group consisting of : polyimides comprising groups delivered from benzophenone tetracarboxylic anhydride (BTDA), methylene diisocyanate (MDI) and toluene diisocyanate (TDI), and polyimides of structure: ##STR00013##

### Current US Cross Reference Classification - CCXR (1):

210/500.39

### Other Reference Publication - OREF (4):

J. H. Fang, H. Kita, K. Okamoto, Hyperbranched polyimides for gas separation applications. 1. Synthesis and characterization, Macromolecules, 33 (2000) 4693. cited by other

### Other Reference Publication - OREF (6):

A. Bos, I. G. M. Punt, M. Wessling, H. Strathmann, Plasticization-resistant glassy polyimide membranes for CO/CH separations, Separation and Purif. Tech. 14 (1998) 27. cited by other

### Other Reference Publication - OREF (9):

Y. Liu, R. Wang, T. S. Chung, Chemical cross-linking modification of polyimide membranes for gas separation, J. Membr. Sci., 189 (2001) 231. cited by other

### Other Reference Publication - OREF (10):

H. Kita, T. Inada, K. Tanaka, K. Okamoto, Effect of photocrosslinking on permeability and permselectivity of gases through benzophenone-containing polyimide, J. Membr. Sci. 87 (1994) 139. cited by other

### Other Reference Publication - OREF (11):

Y. Liu, C. Y. Pan, M. X. Ding, J. P. Xu, Gas permeability and permselectivity of polyimides prepared from phenylenediamines with methyl substitution at the ortho position, Polymer Int., 48 (1999) 832. cited by other

### Other Reference Publication - OREF (12):

Y. Liu, M. X. Ding, J. P. Xu, Gas permeabilities and permselectivity of photochemically cross-linked **polyimides**, J. Appl. Polym. Sci. 58 (1995) 485. cited by other

**Other Reference Publication - OREF (13):**

C. Staudt-Bickel, W. J. Koros, Improvement of CO<sub>2</sub>/CH<sub>4</sub> separation characteristic of **polyimides** by chemical crosslinking, J. Membr. Sci. 155 (1999) 145. cited by other

**Other Reference Publication - OREF (14):**

M. Al-Masri, H. R. Kricheldorf, D. Fritsch, New **polyimides** for gas separation, 1. **polyimides** derived from substituted terphenylenes and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, Macromolecules, 32 (1999) 7853. cited by other